Temperature

°C, K
measure of average KE of motion of particles

Heat
kJ, kcal (Cal) [1 kcal = 4.184 kJ]
measure of total energy transferred from an object of high E → low E

Note: A change in T is accompanied by a transfer of heat energy.

Specific heat (c or cp):
(amount specific for each substance)

\[ q = cp \times m \times \Delta T \]

Units: heat absorbed or released, in J;
\( \Delta T \) in °C or K; m in g; c in J/g°C

Molar heat capacity = heat capacity in J/mol-°C instead of J/g-°C

Don’t forget: the size of 1°C = 1 K, so K can be used in this calculation in place of °C.

Examples

1. How much heat energy is released to your body when a cup of hot tea containing 200. g of water is cooled from 65.0°C to body temperature, 37.0°C? \((c_p \text{ of H}_2\text{O} = 4.18 \text{ J/g}°\text{C})\)

2. A 4.50-g nugget of pure gold absorbed 276 J of heat. What was the final temperature of the gold if the initial temperature was 25.0°C? \((c_p \text{ of gold} = 0.129 \text{ J/g}°\text{C})\)

3. A 155-g sample of an unknown substance was heated from 25.0°C to 40.0°C. In the process, the substance absorbed 5696 J of energy. What is the specific heat of the substance?
Heats of __________

The change in heat energy which occurs during a variety of processes can be described as \( \Delta H \), where \( x \) = process

\[ \Delta H = \text{change in enthalpy (i.e. change in the amount of heat)} \]

\[ \Delta H_{\text{comb}} = \text{heat of combustion (kJ/mol)} \]
energy released when 1 mol of a substance undergoes complete combustion

\[ \Delta H_{\text{fus}} = \text{heat of fusion (kJ/mol)} \]
energy needed to melt 1 mol of a substance

\[ \Delta H_{\text{vap}} = \text{heat of vaporization (kJ/mol)} \]
energy needed to boil 1 mol of a substance

\[ \Delta H_{\text{rxn}} = \text{heat of reaction (kJ)} \]
heat energy absorbed/released during a reaction

\[ \Delta H_f^o = \text{heat of formation (kJ/mol)} \]
energy absorbed/released during synthesis of 1 mol of a compound from its elements at 298 K and 1 atm pressure

\[ \Delta H_{\text{sol}} = \text{heat of solution (kJ)} \]
energy absorbed/released when substance is dissolved in a solvent

Calorimetry

Instrument: bomb calorimeter

1. Put dried food sample in “bomb”.
2. Burn it.
3. Use \( \Delta T \) of water to calculate \( \Delta H_{\text{comb}} \) of the food.
4. The amount of energy in food is measured in Cal, rather than kJ.
5. 1 Calorie = 1 kcal = 4.184 kJ

Basis: \( q = c_{\text{H}_2\text{O}} \times m_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}} \)

Step 1. Calculate \( q \) from calorimeter data.
Step 2. Relate \( q \) to the quantity of substance in the calorimeter.

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Examples

1. What is the heat of combustion, $\Delta H_c$, of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, if 1.500 g of sugar raises the temperature of water (3.00 kg) in a bomb calorimeter from 18.00°C to 19.97°C? ($c_p$ of H$_2$O = 4.18 J/g°C)
   (A: 16.5 kJ/g sucrose, 5650 kJ/mol sucrose)

2. You burned 1.30 g of peanuts below an aluminum can which contained 200.0 mL of ice water ($D_{\text{H}_2\text{O}} = 1.00$ g/mL). The temperature of the water increased from 6.7°C to 28.5°C. Assume all of the heat energy produced by the peanuts went into the water in the can. ($c_{p\text{H}_2\text{O}} = 4.18$ J/g°C). What was the energy content of peanuts, in kJ/g (i.e. $\Delta H_{\text{comb}}$ of peanuts?)
   (A: 14.0 kJ/g)

We can also measure the energy changes when using solutions. In this case the water in which the solutions are made is the surroundings into which heat flows or is removed from.

Sample Exercise 5.7 (p.184)

When a student mixes 50. mL of 1.0 M HCl and 50. mL of 1.0 M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0°C to 27.5°C. Calculate the enthalpy change for the reaction, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100. mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g-K.

(-54 kJ/mol)
Practice Exercise 2 (5.7)

When 50.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30°C to 23.11°C. The temperature increase is caused by the following reaction:

\[
\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})
\]

Calculate \(\Delta H\) for this reaction, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g·°C.

\((-68 \text{ kJ/mol})\)

We can use the heat capacity of the bomb calorimeter itself, as in these next problems:

Sample Exercise 5.8 (p. 185)

Methylhydrazine (CH₆N₂) is commonly used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces N₂(g), CO₂(g), and H₂O(l):

\[
2 \text{CH}_6\text{N}_2(\text{l}) + 5 \text{O}_2(\text{g}) \rightarrow 2 \text{N}_2(\text{g}) + 2 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})
\]

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00°C to 39.50°C. In a separate experiment the heat capacity of the bomb calorimeter is measured to be 7.794 kJ/°C. What is the heat of reaction for the combustion of a mole of CH₆N₂ in this calorimeter?

\((-1.30 \times 10^3 \text{ kJ/mol CH}_6\text{N}_2)\)
Practice Exercise 2 (5.8)

A 0.5865-g sample of lactic acid (HC₃H₅O₃) is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10°C to 24.95°C. Calculate the heat of combustion of

a) lactic acid per gram (-15.2 kJ/g) and

b) per mole (-1370 kJ/mol)

Thermodynamics Word Problems Using Heats of _____ Data

Two of the following three factors will be given:
- amount of substance of interest (usually in grams),
- heat of _____ for the substance
- total kJ

Examples

1. Calculate the heat required to melt 25.7 g of solid methanol at its melting point.
   \( \Delta H_{\text{fus}} \) of methanol = 3.22 kJ/mol
   1. Convert mass of methanol to moles.
   2. Multiply moles of methanol by \( \Delta H_{\text{fus}} \).
   (A: 2.58 kJ)

2. How much heat is needed to vaporize 343 g of acetic acid (CH₃COOH)?
   \( \Delta H_{\text{vap}} \) = 38.6 kJ/mol
   (A = 220. kJ)
Calculating Energy changes using $\Delta H_x$ Lab Data

1. Measure total # kJ (calorimetry), using $q = c_p \times m \times \Delta T$
2. Measure mass of substance, e.g. paraffin lost when candle is burned
3. Divide #kJ by mass of substance of interest $\rightarrow$ kJ/g
4. Convert to kJ per mole by performing a mass $\rightarrow$ mole conversion:

Combustion of a Candle Lab: What is the $\Delta H_{\text{comb}}$ of paraffin wax?

1. Measure total # kJ using $q_{\text{H}_2\text{O}} = c_{\text{pH}_2\text{O}} \times m_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}$ (i.e. $q$ of water in can)
2. Measure mass of substance: $m_{\text{wax burned}} = m_{\text{candle+card before and after expt.}}$
3. Divide # kJ by mass of substance: $\#1 \rightarrow \#2 \rightarrow$ kJ/g (note units include both kJ and g)
4. Convert to kJ/mol using mass $\rightarrow$ mole conversion

Temperature Changes of Water

1. Calculate the energy required to melt 8.5 g of ice at 0°C. The molar heat of fusion for ice is 6.02 kJ/mol.
   A: 2.8 kJ

2. Calculate the total energy change (in kJ) required to
   a) heat 25 g of liquid water from 25°C to 100°C, then
   b) change it to steam at 100°C.
   $c_{\text{pliquid water}} = 4.18 \text{ J/g}^\circ\text{C}$, $\Delta H_{\text{vapH}_2\text{O}} = 40.6 \text{ kJ/mol}$.
   A: a) 7.8 kJ
   b) 56 kJ
   Total = 64 kJ
Thermochemical Stoichiometry

The amount of energy (in kJ) can be incorporated into mole ratios.

\[ \text{e.g. } \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + 6 \text{ O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\text{l}) + 2870 \text{ kJ} \]

\[ \Delta H = -2870 \text{ kJ/mol glucose} \]

Note that because $\Delta H$ is a negative number, the kJ go on the products side of the equation. Note that the number of moles has an unlimited number of sig figs while you must take the number of sig figs in the energy term into consideration.

Examples of mole ratios derived from the above equation:

\[
\begin{align*}
1 \text{ mol C}_6\text{H}_{12}\text{O}_6 & \quad 6 \text{ mol CO}_2 & \quad 2870 \text{ kJ} & \quad 6 \text{ mol H}_2\text{O} \\
6 \text{ mol O}_2 & \quad 6 \text{ mol H}_2\text{O} & & 1 \text{ mol C}_6\text{H}_{12}\text{O}_6 & \quad 2870 \text{ kJ}
\end{align*}
\]

Example Problems:

1. How much energy (in kJ) will be released when 675 g of glucose is burned?
   (A: 10,800 kJ)

2. If 398 kJ is released when a certain amount of glucose is burned, how many grams of oxygen are consumed?
   (A: 26.6 g)

3. If 5782 kJ is released when a certain amount of glucose is burned, how many liters of carbon dioxide are released, assuming the reaction takes place at STP?
   (A: 271 L)
**Enthalpy**

*enthalpein = to warm (Greek)*

Enthalpy (H) = total amount of energy a substance contains

Enthalpy change (\(\Delta H\)) = comparison between enthalpy of products and reactants in a chemical equation

\[ \Delta H = H_{\text{products}} - H_{\text{reactants}} \]

\(\Delta H_{\text{rxn}} = +\) if endothermic:  energy of products > energy of reactants, heat from surroundings \(\rightarrow\) system

\(\Delta H_{\text{rxn}} = -\) if exothermic:  energy of reactants > energy of products, heat from system \(\rightarrow\) surroundings

\[ 2 \text{ H}_2 + \text{ O}_2 \rightarrow 2 \text{ H}_2\text{O} + 483.6 \text{ kJ} \]

\(\Delta H = -483.6 \text{ kJ}\)

**Hess’s Law**

The total enthalpy change for a chemical or physical change is the same whether it takes place in one or several steps.

- “state function”

Version 1: Add equations together

Version 2: Use heats of formation (\(\Delta H_f^0\)) of products and reactants

**Example:**

What is the change in enthalpy for converting graphite to diamond?

**Given:**

\[ \begin{align*}
\text{C}_{\text{(graphite)}} + \text{O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H = -393.5 \text{ kJ/mol C} \\
\text{C}_{\text{(diamond)}} + \text{O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H = -395.4 \text{ kJ/mol C}
\end{align*} \]

**Step 1:** Write rxn.  \(\text{C}_{\text{(graphite)}} \rightarrow \text{C}_{\text{(diamond)}}\)

**Step 2:** Add up rxns to get total rxn, canceling similar terms.

\[ \begin{align*}
\text{C}_{\text{(graphite)}} + \text{O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H = -393.5 \text{ kJ/mol C} \\
\text{CO}_2(g) & \rightarrow \text{C}_{\text{(diamond)}} + \text{O}_2(g) \quad \Delta H = +395.4 \text{ kJ/mol C} \\
\hline
\text{C}_{\text{(graphite)}} & \rightarrow \text{C}_{\text{(diamond)}} \quad \Delta H = +1.9 \text{ kJ/mol C}
\end{align*} \]

**Note:**  **Focus is on the \(\Delta H\).**  **Adding equations is the way you get there.**
Calculate the heat of formation of pentane (C\textsubscript{5}H\textsubscript{12}).

**Given:**

\[
\begin{align*}
    \text{C(s) + O}_2(g) \rightarrow \text{CO}_2(g) & \quad \Delta H = -393.51 \text{ kJ/mol} \\
    \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) & \quad \Delta H = -285.83 \text{ kJ/mol} \\
    \text{C}_5\text{H}_{12} + 8 \text{O}_2(g) \rightarrow 5 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) & \quad \Delta H = -3536.1 \text{ kJ/mol}
\end{align*}
\]

**Final equation:** \(5 \text{C(s) + 6 H}_2(g) \rightarrow \text{C}_5\text{H}_{12} \quad \Delta H^o_f = ?\)
Hess’s Law (Version 2)

The enthalpy change of a rxn is equal to the heats of formation of the products minus the heats of formation of the reactants (and taking stoichiometric relationships into account).

\[ \Delta H = \Delta H_f^o \text{(products)} - \Delta H_f^o \text{(reactants)} \]

**Example**

Calculate the change in enthalpy for this reaction:

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

Given:

\[ \Delta H_f^o \text{CO}_2 = -393.5 \text{ kJ/mol} \]
\[ \Delta H_f^o \text{H}_2\text{O}(l) = -285.8 \text{ kJ/mol} \]
\[ \Delta H_f^o \text{CH}_4 = -74.86 \text{ kJ/mol} \]
\[ \Delta H_f^o \text{O}_2 = 0 \] (Note: \( \Delta H_f^o \) of free elements = 0)

**Step 1:** Calculate the total \( \Delta H_f^o \) for the products and the reactants.

\[ \Delta H_{\text{products}} = (-393.5 \text{ kJ})(1 \text{ mol} \text{ CO}_2) + (-285.8 \text{ kJ})(2 \text{ mol} \text{ H}_2\text{O}) = -965.1 \text{ kJ} \]
\[ \Delta H_{\text{reactants}} = (-74.86 \text{ kJ})(1 \text{ mol CH}_4) = -74.86 \text{ kJ} \]

**Step 2:** Plug these values into the following equation.

\[ \Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}} = -965.1 \text{ kJ} - (-74.86 \text{ kJ}) = -890.2 \text{ kJ} \]

**Practice:**

Use standard enthalpies of formation from Appendix C to calculate \( \Delta H_f^o_{\text{rxn}} \) for the following reaction:

\[ 4 \text{NH}_3(g) + 7 \text{O}_2(g) \rightarrow 4 \text{NO}_2(g) + 6 \text{H}_2\text{O}(l) \]

(A: -1397.9 kJ)
Why don’t exothermic reactions occur spontaneously (e.g. with no spark)?
Energy is needed to overcome the mutual repelling of the atoms involved in the reaction.
Activation energy ($E_a$) = initial output of energy
Note: Different reactions have different activation energies.

**Reaction Profiles**

**Exothermic Reaction**

(a) Activation energy
(b) Energy released by activated complex
(c) $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$

**Endothermic Reaction**

(a) Activation energy
(b) Energy released by activated complex
(c) $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$